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	PROJECT 325B SUMMARY REPORT	
	PERIOD: 1 March 1972 to 31 March 1972	
	Submitted By: Project Manager	25X1
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	SUMMARY	

March saw many of the problems of equipment and darkroom availability finally resolved. The new engineering darkroom was completed and placed in use. All laboratory bench chambers were either received in proper working order or placed in such a posture. Heavy emphasis was underway at the last part of the month on those tasks requiring this equipment or darkroom; decay studies in pure atmospheres and reactivation studies.

A complete three month briefing was assembled for delivery at the Customer's facility the tenth of April. This briefing includes color slides of the Engineering darkroom and new project equipment.

It was not possible to complete the qualification of the Quantametric automatic plotting densitometer as the project standard during March because of problems with positioning of the small project step wedges, and attention to other work areas by the project team. It is hoped the qualification can be completed in the near future.

CHEMICAL R AND D

Overview

D260-anthrone has been identified as an impurity in D260. It has been demonstrated to be an oxidation product of D260. The anthrone, also an intermediate in the alternate D260 synthesis, has been successfully synthesized.

Solution interaction decay studies have shown that D260 decays in the absence of 4PO and/or D7, that 4PO significantly stabilizes this decay and that D7 severely interacts with D260.

Carbon tetrabromide deterioration studies proceed but were delayed due to failures in the environmental glove boxes. These failures have not seriously affected the study.

Two tribromoacetophenone derivatives have shown promise as potential activators.

The N-oxide program, Phase II, has been indefintely postponed. This is a result of the first 2-1/2 month manpower shortage combined with the current need for emphasis elsewhere and the fact that Phase II is not currently seen as critical to the immediate speed decay problem.

Styron 685 and 686 are suitable substitutes for MX4500.

The additive/impurity concentrate of MX4500 is detrimental to sensitometric properties.

Studies have been initiated on the effect of the binder's molecular weight on sensitometric and speed decay properties.

Work has begun on the 5/DPA film system.

Results of the air analysis program are complete. The prior correlations of "bad" film with oxidants and possibly acids is now more uncertain.

The speed decay phenomenon has been shown to be due to loss of primary sensitivity and compounded by complications in red lite development mechanisms.

Dark fogging is discussed as a current anomaly in speed decay.

1.0 CHEMICAL R AND D

1.1 Leuco Dye Program

1.1.1 D260

About 1 kg of D260 was received from Chemical Samples Coduring March. This material is described as crude but is free of TMB as determined by the usual TLC procedure. Several other impurities are detectable however, when the TLC plate is developed with iodine in the usual manner. Of considerable interest was the discovery of an intensely fluorescing spot, trailing the D260 when an undeveloped plate is viewed with long wavelength UV light. The fluorescence is not seen with a developed plate.

The impurity was isolated by elution chromatography which was greatly facilitated by the newly acquired automatic fraction collector.

Use of the collector resulted in the isolation and identification of this impurity within one working day. The impurity was found to be the D260-anthrone as authenticated by comparison to anthrone synthetically prepared as part of the alternate D260 synthesis. After attempting a number of purifications on small (2-10 g) samples of this D260, it was found that trituration with ethyl ether followed by recrystallization from cyclohexane yielded the best grade and largest amount of D260. For example, 400 g of crude D260 were triturated with 500 ml of ethyl ether, filtered and washed with an additional 500 ml of This blue solid was virtually ether to give 293 g (73.4%). It was then dissolved in 3550 ml of boiling free of anthrone. cyclohexane and treated with 29 g of Norit A, filtered through 293 g of cellulose and chilled in ice water and the resulting white solid collected by filtration go give 208 g (71%, 52% overall) of material containing a trace of anthrone.

Work was then continued with small samples of this batch to further improve purity. For example, trituration with both cold and warm ethyl ether failed to remove further fluorescence. Solution in benzene and elution through basic alumina reduced markedly the amount of anthrone present, but it was noted that this solution on standing in light and air for several hours increased dramatically in anthrone content. Recrystallization

from cyclohexane and solution through basic alumina failed to change sample quality. This same sample on solution in benzene, followed by concentration and precipitation of D260 by petroleum ether gave back material showing more anthrone than the original sample.

Another sample triturated with ether in an argon atmosphere also did not improve in quality. Wash of this sample both with 10% aqueous bicarbonate and 1 N sodium hydroxide gave two samples with no fluorescence in the anthrone region of the TLC plate but a trace of impurity is present just prior to that region.

Those instances where anthrone could not be entirely removed or where the processed material contained more anthrone than at the start, suggest that the anthrone is being formed during processing. If this is so then the presence of D260-hydroperoxide seems necessary to explain the formation of the anthrone. The simultaneous formation of 4DMAP would serve to remove nearly any doubt that the hydroperoxide is present. However, we do not as yet have a suitable means for detecting the simultaneous presence of 4DMAP with anthrone.

Work continues to develop the most efficient means for purifying D260, to understand the role of impurities in complicating the purification and to determine their effect on film properties.

1.1.1.1 Alternate Synthesis of D260 - The Anthrone Route

The details of the anthrone route were shown in the January report.

D263 (10 g) was converted to the crude nitrate dye and oxidized with lead dioxide paste to 3.9 g of crude anthranol (37%). Following Aaron and Barker's procedure closely, the crude anthranol with benzophenone in potassium t-butoxide gave 0.55 g crude anthrone. This was once recrystallized from ethanol to give 0.3 g of pale green crystals, mp 210.5-213°C (lit.: 207-208°C plus a second, less pure crop of 0.45 g). Yield from D263 to recrystallized anthrone: 7%.

The low yield is attributed to changes in workup and oxidation procedure from D263 to anthranol. A rerun of this two-step reaction will be carried out in order to optimize this procedure.

1.1.1.2 Analogues of D260

Once the procedure for good anthrone is optimized, it is planned to react it with three organolithiums to make D260 and two D260 analogues, the malachite green analogue, and D423 as shown.

1.
$$(CH_3)_2N$$
 $+$ $(CH_3)_2N$ $+$ $(CH_3)_2N$

D243 is a known compound and is a dye former of Horizons' vinylidine class. In a general sense this compound can be considered a dye-base like D7 since reaction with acid serves to produce a dye. In this instance the dye is of the diphenylmethane class rather than the cyanine class of D7. The dye of D423 reportedly has an extinction coefficient some ten times greater than the cyanine types and D423 itself is expected to be more readily soluble than D7. Primarily for these reasons D423 will be investigated as a replacement for D7.

1.1.1.3 Short Route to Anthrone

In an effort to get anthrone more directly, p-dimethyl-aminobenzoic acid was reacted with m-isopropenyldimethylaniline in polyphosphoric acid, but anthrone could not be detected.

It seems probable that the olefin function polymerized in the presence of the Lewis acid.

1.1.1.4 Role of D260 in Speed Decay - Ingredient Interaction Decay Studies

In order to determine any interaction taking place between D260 and any other component of the 5/D7 system, four solutions were prepared and allowed to stand in the dark at ambient temperature. The four solutions contained the following components:

At measured intervals, aliquot samples were removed and coated. The remaining components were added just prior to coating. Film results can be found in Table 1.

The results show the usual variations which can be expected over a period as long as 34 days. In spite of these variations the trends are unmistakable as seen in Figures 1 through 4.

Figure 1 (Solution 1: D260) shows definite decay to the point where no net image is obtained somewhere between 20 and 34 days. Note the very significant increase in development time which was limited to a maximum of 300 seconds in order to

avoid excessive strain on the HID-2 development unit. This establishes the fact the D260 can decay without the assistance of 4PO and/or D7.

Figure 2 (Solution 2: D260, 4PO) illustrates a marked stabilizing effect by 4PO. The decay rate is slowed considerably with a still reasonably good net image and a measureable AEI of 1.0 after the same 34 days. Note that the rate increase in development time has also been significantly reduced.

Figure 3 (Solution 3: D260, D7) shows a severe interaction with D7. The solution shows a very rapid decay with no net image after 14 days; only a uniform magenta fog. Note the correspondingly rapid increase in development time. D7 is a dye base and is readily converted to its corresponding dye by acid. An obvious initial inference concerning the D260/D7 interaction would therefore be that acid is being formed and producing unwanted D7-dye. This cannot be the cause, however, since acid contamination has been shown to drastically shorten development time whereas Solution 3 showed a rapid increase in time. Besides, further aging to 20 days and beyond afforded not a magenta fog but a faint blue fog with the same maximum development time of 300 seconds. This indicates that the reaction(s) which produce D7 dye during development has been prevented, or at least severely retarded. Finally it was noted that at 34 days Solution 3 had turned from colorless to green. The yellow of D7 combined with the blue of D260-dye accounts for the green Since only this solution turned color it appears that D7 enhances either the oxidation of D260 itself or subsequent D260-dye forming reaction(s). The clear green color also rules out any appreciable quantity of D7-dye which in turn implies that no appreciable acid is formed during the decay.

Figure 4 (Solution 4: D260, D7, 4P0) again illustrates the significant role played by 4P0. The severe interaction between D260 and D7 has been moderated to the point that the photographic properties are very similar to Solution 1 (Figure 1).

Results of the ingredient interaction aging study raise several other points in addition to those already discussed.

First, comparison of these decay rates to the two hour decay rate of the 5/D7 Coating Solution illustrates the significant effect the activator, CBr_4 , has on speed decay. This is perhaps not surprising since the function of activator is after all to sensitize the system. Just the same, it is possible

that the effect of CBr₄ is not merely a magnification of decay but rather the introduction of additional decay through a catalytic impurity, for example, that impurity which apparently is the cause of solid state deterioration of the CBr₄.

Second, the decay of solution does not imply inherent decay properties for D260. The effect of solvent and binder must first be determined. Work was initiated with this objective in mind. However, due to equipment failure the work had to be temporarily discontinued, but it is expected to resume in April.

Finally, this study and its results imply that such bulk solution decay studies relate to the speed decay phenomenon exhibited by the film. This seems altogether a reasonable assumption to make as evidenced by the fact that decay in bulk solution does occur. This fact itself rules out the possibility that speed decay of film is solely a phenomenon of thin In fact, the bulk coating solution decays at a rate only two to four times slower than the corresponding film. the various decays which are observed may be due to the same ultimate cause in which case a further detailed study of Solution 1 should serve to identify that cause(s) without the complications of other ingredients. It must be realized that one or more of these decays may be due to independent causes. For example, Solution 1 decays as a result of one cause while Solution 3 decays due to that cause plus another one which is in some way related to D7.

The results to date raise a number of pertinent questions, some of which are:

- 1. Is Solution 1 decay due to interaction of D260 with oxygen in the air, as is presupposed if the D260-hydroperoxide hypothesis is correct¹?
- 2. Is said interaction an inherent property of the D260 molecule or is it catalyzed by an impurity in D260?
- 3. Is said interaction effected by the solvent benzene and/or the polystyrene binder and if so are they due to inherent properties of chemical structure or due to impurities which, for example, are known to be present in the polystyrene (cf. Section 1.4.2)?

- 4. Is the interaction of D7 due to inherent chemical structure or to an impurity in D7?
- 5. Is the D260/D7 interaction direct or indirect; that is, through an intermediate reaction between D7 and solvent and/or binder?
- 6. How does 4PO moderate the D260 decay? Does it retard decay, intervene in a subsequent reaction or perhaps tie-up an otherwise catalytic impurity?

It is by answering questions such as these that we plan to ultimately identify the specific problem areas, so that a reasonable solution to the speed decay problem can be found. Answers to some of the above questions are already available and will be discussed at a later date. For the most part, however, these questions and others remain currently unanswered. In nearly every instance the question of impurities arises and it is for this reason that the matter is and will continue to receive emphasis. Included is the question of external or environmental contamination and this matter will be further discussed in Section 1.5.

1.1.2 Other Leuco Compounds

Synthesis work has continued and several new LCV-analogues have been prepared.

With the hiring of the two new organic chemists, this month's work on purification and film evaluation of other leuco compounds has been resumed. Some preliminary results are available but discussion will be deferred to the April report when a more complete discussion will be possible.

1.2 Carbon Tetrabromide (CBr₄)

The CBr₄ program continues essentially on schedule with only minor delays. Plans to purify Freeman and BDH CBr₄ from solvents other than petroleum ether as well as from an oxygen-free environment have been postponed as a result of both the 2-1/2 month manpower shortage and environmental contamination. The plan was to supplement the CBr₄ deterioration studies as a

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means of establishing the cause(s) of CBr₄ solid state deterioration. The solid state deterioration program is underway as outlined in Chart I, page 16 of the February Summary Report. The results of that study should be sufficient to identify the cause(s) of the deterioration. Thus, the above mentioned plans can be still further delayed without any immediate consequence. Results of the deterioration study may even permit abandonment of these plans, but it is still too early for such a decision.

1.2.1 Deterioration Studies

These studies were initiated last month as stated above. A breakdown of two LabConco glove boxes which contained a purified synthetic air $(80\%\ N_2,\ 20\%\ 0_2)$ atmosphere, under which these studies were being conducted, prevented film evaluations from being made during most of March. The various samples remain intact and the evaluation will continue as of early April without serious consequence to the deterioration studies. The only possible consequence of these breakdowns will be in establishing the exact date of noticeable deterioration, should any of the samples be found to have deteriorated during March. Even in such an instance the most important fact would be whether or not a given sample has decayed. Thus, the indicated delays here and in the preceding section have not seriously affected the program.

1.2.2 Hexabromoethane (C_2Br_6)

A concentrated sample of hexabromoethane has been isolated from "bad" CBr_4 and has been found to contain higher analogues. Mass spectral analysis indicates less than 1% decabromobutane, $\operatorname{C_4Br}_{10}$ as well as less than 1% pentrabromochloroethane, $\operatorname{C_2Br}_5\operatorname{Cl}$. These analogues have not been isolated nor evaluated but it would be very improbable that they are the cause of the deterioration of solid CBr_4 or the cause of "bad" films. They undoubtedly arise by the same reactions that form $\operatorname{C_2Br}_6$ ($\operatorname{C_2Br}_4\operatorname{Cl}$ coming from the $\operatorname{CBr}_3\operatorname{Cl}$ known to be present as a benign impurity in CBr_4).

1.2.3 Other Sources of CBr4

A 5 kg sample of CBr_4 was received from Koch-Light of England. It is pale yellow in color. To avoid atmospheric

contamination it has not yet been opened, but rather is being kept for use upon reestablishment of the purified atmosphere in the glove boxes.

1.2.4 Other Activators

Tribromoacetophenones have been used as activators in other leuco systems

Two such compounds, α , α -tribromo-2,5dimethylacetophenone (I) and α , α -tribromo-4-nitroacetophenone (II) were on hand and were therefore evaluated with 5/D7. Both were purified by recrystallization from methanol.

Both I and II were used in place of CBr₄ (200 mg was upper limit of their solubilities) and as additives (50 mg) to the standard 5/D7 formulation (Table 3). In all instances development resulted in total fog with no discernible image. Printouts gave significant imagery, with I superior to II. II appears to afford D7-dye as evidenced by the reddish or deep purple fog. I apparently reacts only slightly if at all with D7.

The results indicate these materials are activators though whether they would serve for the development mode remains uncertain because of their unknown states of purity. Remember that "bad" CBr₄ behaves similarly in giving high development fog with little or no imagery.

No further work is currently planned, but the promising results to date will certainly lead to further investigation at a later date.

1.3 N-Oxide Program

Further work has been indefinitely postponed due to the need for emphasis elsewhere. The analysis of Phase I results is nearing completion and should be available for the April Summary Report.

1.4 Binder Studies

1.4.1 Substitutes for MX4500

The December Summary Report (page 3) mentions the beginning of studies to evaluate Styron 685 and Styron 686 as possible substitutes for MX4500, which is no longer available. The studies involved evaluating 5/D7 using standard 10% benzene solutions and included evaluating the possible aging of the corresponding activator solutions. After fourteen weeks of evaluation we conclude that either the 685 or the 686 can be used as a suitable substitute for MX4500. The results are seen in Table 2.

1.4.2 Effects of Binder Impurities/Additives

Three commercial grade polystyrenes were sent to Water's Associates, Inc. (Framingham, Mass.) for concentration of the low molecular weight fractions which contain the commercial additives and impurities. The separations were done by gel permeation chromatography and the impurities and/or additives are readily discernible in the UV absorption profiles of the eluents. The three polymers were MX4500, the standard for this project; Borden's 230,000 which appears to give slightly poorer film results; and Lustrex which gives decidedly poorer results. Water's Associates returned benzene solutions of the concentrated fractions as obtained directly from the column. These fractions contained at most only milligrams of material and the MX4500 concentrate appeared to contain the most.

The benzene was removed from the MX4500 concentrate and the residue added to films made with Pressure Chemical's 200K standard . Pressure Chemical's 200K is a standard polystyrene polymer of known molecular weight (200K) and narrow molecular weight distribution (Mw/Mn = 1.06). It contains no additives and was chosen as the polystyrene binder because of its similar physical characteristics and chemical behavior to MX4500 3 .

The addition of the MX4500 concentrate is indeed detrimental as seen from the results shown in Table 4. Net densities are lowered and development times are extended. Even 5 mg has a significantly detrimental effect.

The concentration of impurities/additives represented by the 5 mg of concentrate is certainly higher than that present in standard 10% MX4500 solution. The results suggest, however, that MX4500 might be giving less than optimum possible results due to the level of impurities/additives which is present. On the other hand, comparison of Pressure Chemical's 200K with MX4500³ shows no significant difference. This indicates no detrimental effects on sensitometric properties at normal MX4500 impurity/additive levels.

The possible effects on speed decay have not yet been studied, however. These studies as well as the relative effects of Borden's 230,000 and Lustrex additives/impurities will be studied at a later date when the current materials' purity and environmental contamination problems are under better control.

1.4.3 Effect of Molecular Weight on Photographic Properties

Work has begun on studying the effect of molecular weight on photographic properties including speed decay. This subject will be discussed in the April summary report.

1.5 Environmental Studies

1.5.1 Air Sampling

The remainder of data from the air analysis program has now been received and the complete results are tabulated in Table 5. The latest results make the initial correlations with oxidants and possibly hydrogen halides even more uncertain.

The program was terminated on February 29, 1972. At this time there are no specific plans for further air analysis studies (cf. Section 3.7).

1.5.2 Preliminary Environmental Film Studies

The original plan to initiate, in March, studies in materials' purity on film properties, under controlled environmental conditions, has been seriously delayed. This delay has resulted from delays in obtaining the necessary glove boxes and compounded by the delivery of several faulty boxes.

The poor experience with LabConco boxes resulted in the cancellation of an order for two such boxes and the purchase of a single Kiwanee Model glove box. This box is superior in every way and will be quite adequate for formulating, coating and exposing film within.

It is now expected that work will begin in the middle of April. It is currently estimated that this program will have slipped from one to two months by the time it is fully underway.

1.6 Other Film Systems

This program has been delayed due to environmental contamination of Chemical R and D's second darkroom where this work will be performed. Attempts to decontaminate this room were discussed in last month's report⁴ and the results were encouraging. As a result some preliminary work with 5/DPA was initiated toward the end of March. The results of this work will be discussed in the April Summary Report.

1.7 Film Analysis of Decay Products

This program has not been initiated due to the earlier manpower shortage. This delay is not deemed serious to the overall effort since only recently have suspected decay products of D260 been detected and identified from non-film work. These non-film results should simplify the film decay studies since specific decay products can be sought. Thus, the rather small effort which has been lost from January through March should be recouped before the end of June.

1.8 Dye Identification

Nothing to report.

1.9 System Nonuniformities

Nothing to report.

1.10 Miscellaneous Studies and Discussions

This is a new section which is being added for reporting and discussing work, which although performed as part of one or more of the other work areas, is best discussed as a separate entity.

This section is not a new task and will not be treated as a separate line item. Its purpose is merely to provide a place for isolating and discussing various aspects of the shelf life/speed decay problem, which if included in one or more of the other sections would detract from a clear and concise report of progress within those sections.

1.10.1 Formula 5/D7 Aging Studies - Exposure Variation

A continuing question concerning rapid speed decay has been whether the phenomenon is associated with loss of primary sensitivity, in other words, with the loss of ability to record latent image, or whether the phenomenon is primarily associated with complications in the red light development mechanisms. As previously described, the development mode shows practically total loss of imaging capability within one hour at room temperature. The printout mode which is a measure of primary sensitivity, on the other hand, shows some decay after about three hours (there is apparent decay after one hour but results are within normal experimental error). These facts leave no doubt that loss of primary sensitivity occurs but suggest that this loss is too slow to account for the rapid decay observed in the development mode.

Experiments were performed which now establish that the observed rapid speed decay is due to loss of primary sensitivity coupled with a probably severe interference of the red lite development mechanism.

1.10.1.1 Printout Exposure

Figure 5 compares printout D-log E curves of films aged 3 to 3-1/2 hours to freshly coated film (age ca. 75 seconds). Comparison of Curve 2 with the control, Curve 1, shows the significant decay apparent after three hours. The comparison is based upon the standard printout exposure time of 300 seconds (5 minutes). Curve 3 represents a 3-1/2 hour old film resulting from a 900 second (15 minutes) exposure. It can be seen that a

three-fold increase in exposure produces a curve essentially identical to that obtained with undecayed film. The primary sensitivity therefore appears to have decayed by a factor of about three in three hours, assuming self-sensitization does not occur during the exposure (cf. Section 1.10.1.4).

Figure 6 shows a similar experiment conducted after a decay period of 17 to 18 hours. The greater extent of decay is readily apparent as well as some build-up in fog (this fog is referred to as dark fogging and is discussed in Section 1.10.2). A six-fold increase in exposure time to 1800 seconds (30 minutes) produces Curve 3 which is similar to that of unaged film (Curve 1). The curve shape is noticeably different, however. The difference in shape is not unlike normal experimental variations which have been observed, so it cannot be determined at this time whether the difference is due to experimental error or is real. It is probably real since it is reasonable to expect that the chemical changes which have occurred during aging would result in different sensitometry.

1.10.1.2 Latent Image Exposures

The next step was an investigation of the development mode. Figure 7, Curve 1, shows the standard control in which a 1/10 second exposure is made 75 seconds after coating. The film is then immediately developed.

From the same coating a film strip was given a 1/10 second exposure one hour later. The first step was barely discernible with an increase of development time from 50 seconds to 77 seconds, and there was medium fog with some blotch. The exposure was then increased to one second resulting in Curve 2. A further increase to 5 seconds resulted in Curve 3. Its irregular shape is probably due to some "blotching" within the image areas.

Figure 8 shows still another example of a 5-second exposure and development after 2-1/2 hours. Note that in this instance the curve shape is not so irregular.

1.10.1.3 Latent Image Exposure With Delayed Development

To conclude this series of experiments a fresh film was again given a 1/10 second exposure and then allowed to stand for 2-1/2 hours before development. The result is seen in Figure 9.

1.10.1.4 Discussion

These experiments are the first of their type to have been performed. They are necessarily crude and hence any attempt to attribute significance to curve shape is premature. Their significance lies in the following: the nearly total loss of imaging capability (decay) which is observed in the development mode after only one hour of aging at room temperature is only in part due to loss of primary sensitivity, or in other words, is due to the fact that a 1/10 exposure no longer produces sufficient latent image.

The printout mode shows that an approximately three-fold increase in exposure is required after 3-1/2 hours in order to simulate a fresh film. Comparison of Figure 8 with Curve 1 of Figure 7 shows that a fifty-fold increase in latent image exposure after 2-1/2 hours is necessary to produce a curve which is at all comparable to fresh film. If the observable speed decay of the development mode were due solely to loss of primary sensitivity why then a fifty-fold increase in exposure when only a three-fold increase is indicated by printout exposure?

Self-sensitization in the printout mode would be one possible explanation, in that it would afford an apparent decay factor less than the true factor. This possibility is excluded on the basis of past work on the spectral sensitization of formula 7/D7. That work is summarized in Figures 10 and 11. These graphs show the measured sensitivity as a function of exposure time for two different regions where crystal violet absorbs strongly. If the crystal violet formed during exposure were sensitizing the film one would expect to see greater measured sensitivity at longer exposure times (greater exposures). The horizontal graphs show this is not the case. The photographic properties of 7/D7 and 5/D7 are too similar to exclude extention of these results to the 5/D7 system.

It must therefore be concluded that the more rapid decay of the development mode is a manifestation of the complications in the chemistry of the red lite development mechanism. Consider Curve 1 of Figure 7 and Figure 9. The difference in results is due only to delaying development for 2-1/2 hours; the amount of latent image in each instance is equal to a 1/10 second exposure of fresh film. Note that both Dmax and fog are lower for the aged film and with approximately a 50% increase in development time.

In contrast, a 5 second exposure with immediate development after 2-1/2 hours (Figure 8) results in a curve reasonably comparable to the control (Curve 1, Figure 7) again with about a 50% increase in development time. The differences in exposure increases of three times and fifty times can now be explained.

During speed decay the primary sensitivity is lowered by a factor of about three after 2-1/2 hours. If this were the only factor then a latent image exposure increase from 0.1 to 0.3 seconds would be sufficient. However, the development mechanisms is also affected and to a considerably greater extent. It is affected to such an extent that not a 0.3 second exposure is necessary but rather a 5 second exposure. Thus, of the 5 second exposure required to produce Figure 8, 4.7 seconds is necessary to compensate for the affected development mechanism. In other words, as the film decays more latent image is necessary to produce a given image density.

If this argument is basically correct, then an immediate latent image exposure of 4.8 seconds (4.7 compensation plus normal 0.1) should after 2-1/2 hours decay give the curve shown in Figure 8. Unfortunately, this experiment was not performed. It, along with additional refinements of this study, is planned for April and May. Discrepancies have been recognized concerning the description of the speed decay phenomenon. These discrepancies deal with the appearance of a dark fogging not previously recognized. This matter must be clarified before any attempted refinement of decay studies is undertaken. It is the subject of discussion in the next section.

1.10.2 Dark Fogging: A Discrepancy in the Observable Behavior of Speed Decay

Past observations of the speed decay phenomenon showed that after one hour at ambient temperature, the usual exposure of 1/10 or 1/2 second at approximately 200 mc gave at most only a faint image regardless of the extent of development. It was further noted that significant increases in development time, like those shown in Figures 1 to 4, were necessary to produce fog levels comparable to fresh film. In other words, the aged film had decayed with respect to both image and fog development. Since the beginning of Project 325B in January, the same general behavior has been continuously noted with regard to image On the other hand it appears that the tendency formation. for decayed film (one hour) to fog during development is now greater than noted in the past. Unfortunately this apparent observation cannot be quantitatively supported since HID-2 development units with stationary development have been used almost

exclusively on P325B, while previously the older dichroic units with oscillating platens were used. Coupled with this apparent discrepancy was another past observation in which some freshly coated film was placed in a drawer in a darkroom for one or two days, after which time the film had decayed but showed no fog build-up (dark fogging). Again unfortunately, this observation was reported but not recorded and hence cannot be substantiated. In contrast, current decay studies show an increase in fog at ambient storage in our darkrooms. Thus, a freshly coated film if given a printout exposure and then fixed shows no fog and only the normal base density of 0.06 to 0.08. After one day at ambient storage, however, the film

These apparent discrepancies between past observations and current findings is mentioned in order to introduce the suspicion that fogging and speed decay are not the same phenomenon but in fact are independent. The realization of materials's purity problems, particularly D260, and that atmospheric contamination was not a recognized problem in the past, suggest that impurities, either in materials or in the atmosphere, cause fogging independent of the rapid speed decay. At this point, however, such an hypothesis is predicted on a comparison of current fact with cursory observations of the past.

shows, in addition to the image decay, a magenta fog of density

0.20.

Several recent observations do, however, add substantial support of this hypothesis.

First, during our pilot coating efforts of late last year we observed that antioxidants like Plastinox 425 did not alter the rate of speed decay but did cause a significant increase in the rate of ambient, dark fogging. Thus, at least certain materials can cause fogging apparently independent of speed decay!

Most dramatic however are recent observations made in regard to the QC/QA program. Studies have been conducted on various methods of storing film for shipping to P. E. Freshly coated film was immediately packaged and stored on Dry Ice for ten days. The film was then allowed to warm to ambient temperature and has been stored ambient ever since. After four weeks at ambient temperature, fixed pieces of this film show numerous high density spots. Microscopic examination reveals an undissolved crystal of D7 at the center of each spot. This phenomenon has been mentioned previously and is unquestionably associated with the incomplete dissolution of D7. This is the reason why D7 has been cited as one cause of system nonuniformities⁵.

Aside from these high density spots, however, the clean areas of the film show no fog build-up. Thus it would appear that dark fogging and speed decay are indeed independent. is conceivable that the ten days of storage at -30°C has played some role in this observation. Of more immediate interest is the implication that environmental contamination is the cause of fogging. The normal decay studies are performed without isolation from the normal darkroom environment. the QC/QA study, film was isolated from the normal environment while still tacky, by sealing in boxes. Perhaps continual exposure to unknown impurities in the normal environment causes the fogging. The reality of atmospheric contamination has been unequivocally established. The fact that the one chemistry darkroom has constantly afforded good film does not preclude the presence of contaminants at levels sufficient to effect fogging, particularly over an extended period of time.

The question of the independence of speed decay and fogging remains to be positively established. The importance of this question can be appreciated in view of the exposure variation experiments described in Section 1.10.1.

One unquestionable result of these experiments is that development time is significantly increased. It must be concluded, therefore, that whatever chemical reactions are occurring during decay, they in some way interfere with the mechanism of dye formation, be it fog or image. It was also inferred in Section 1.10.1.4 that the rate of image development is more seriously affected than the rate of fog development since net densities are severely reduced. It is, however, possible to explain at least a portion of this difference in rates as a result of dark fogging.

After three hours a normal 0.1 second latent image exposure produces an amount of latent image only three times less than would be the case if the film were fresh, due to the decay of primary sensitivity. However, during this decay period dark fogging though not visually apparent is undoubtedly building to produce a greater latent fog level. As a result of this fact the rate of fog formation during development will be greater in relation to image formation than in the case of a fresh film where latent fog is lower, even though both rates have been retarded. This increase in the ratio of fog rate to image rate is sufficient to reduce the net image to levels considerably lower than would be expected on the basis of a three-fold loss of primary sensitivity. As a result of this latent fog formation, latent image must be increased in order

to obtain a result comparable to a fresh film. Thus, at least a portion of the fifty-fold increase in latent image exposure can be explained by postulating the formation of latent fog during decay.

To what extent latent fog formation may contribute to this large difference between decay of primary sensitivity and of developable (secondary) sensitivity cannot be estimated at this time. If dark fogging and loss of primary sensitivity are indeed independent as the result of the QC/QA packaging studies would suggest, and the ratio of the developable rates of fog to image formation is not otherwise affected, then one would expect to simulate undecayed results by increasing the exposure merely by the factor indicated by the associated printout exposure. Such study could be quite valuable in elucidating greater understanding of the speed decay phenomenon. It must necessarily wait, however, until the phenomenon of dark fogging is more clearly defined.

1.10.3 Summary

It is evident from the foregoing discussions that the mechanism of speed decay may be complex. The arguments which have been presented are necessarily beginnings. Nevertheless they serve as a basis for further investigation and for an ultimately more thorough understanding of this phenomenon.

Loss of primary sensitivity has been shown to occur during speed decay.

The much greater loss of secondary sensitivity (the overall sensitivity as determined by the development mode) has been shown to be apparently unexplainable solely in terms of the loss in primary sensitivity.

Discrepancies concerning a description of the speed decay phenomenon have been described and from these the inference that the phenomenon may be due to several independent causes. In this regard and particularly with respect to dark fogging, the concern over materials' purity and particularly environmental contamination has again been cited. The overall importance of the impurity and contamination areas cannot be over emphasized.

Finally, the results to date would suggest that if dark fogging is in fact independent of speed decay and can be separately prevented, then reactivation by means of a blanket pre-exposure is a possible means of overcoming the speed decay problem.

TABLE 1 5/D7 INGREDIENT INTERACTION DECAY STUDY

Exp. No. 1756-40-	∆T _V Days	?	AEI	Dmax B	Dmin B	Dnet B	ΔT_r sec.
Solution	1: D260	(1756-4	10-1A)	•			
1	_	7.2	.67	2.30	.22	2.08	47
5	1	1.4	.23	1.53	.28	1.25	76
9	2	2.5	.64	2.36	.15	2.21	61
13	3	1.6	1.8	2.30	.33	1.97	69
17	6	1.8	1.4	2.18	.23	1.95	92
23	8	2.0	1.7	2.17	.21	1.96	105
27	10	-		2.22	,30	1.92	124
33 38	14 20	3.0 1.8	1.3 .15	2.47 2.05	.39 .29	2.08 1.76	170 246
43	34	-	-	.10	.10	-	300¹
Solution	n 2: D260), 4 PO (]	1756-40 -2 A)			
2	_	3.0	1.0	2.32	.26	2.06	40
6	1	2.2	1.4	2.22	.33	1.89	47
10	2	3.4	.83	2.41	.24	2.17	45
14	3	1.4	2.3	2.03	.33	1.70	56
18	- 6	2.3	.89	2.09	.26	1.83	80
24	.8	2.6	.66	1.97	.25	1.72	69 77
28 34	10 14	4.6 1.9	.74 1.3	2.46 2.23	.26 .36	2.20 1.87	77 110
39	•20	-	-	2.23	.29	1.90	118
44	34	1.1	1.0	1.96	.48	1.48	270
Solution	n 3: D260), D7 (17	756-40-3A)				
3	-	3.0	1.5	2.23	.26	1.97	43
7	1	2.2	.66	1.76	.24	1.52	56
11	2	2.4	1.3	2.21	.23	1.98	63
15	3	-	-	2.06	.39	1.67	75
19	6	1.1	.83	1.75	.30	1.45	123
25 29	.8	-		2.32 1.75	.43	1.89	163
29 35	10 14	-	-	.37	.45 .37	1.30	220 300 ²
40	20	_	_	.19	.19	_	3003
45	34		-	.12	.12	_	3004
Solution	n 4: D260), D7, 41	0 (1756-4	0-4A)			
4	-	3.3	.67	2.31	.21	2.10	37
8	1	2.5	75	1.95	.20	1.75	50
12	2		-	1.92	.27	1.65	66 ⁵
16	3	1.6	.63	1.96	.27	1.69	73
20	6	1.8	.74	2.05	.33	1.72	119
26	8	1.5	.74	1.91	.23	1.68	135
30 36	10	_	_	2.04	.52	1.52	169
36 41	1 <u>4</u> 20	_	_	$2.14 \\ 2.04$.41 .45	1.73 1.59	220 254
46	34	_	_	.28	.18	.10	300e
	~-					• 0	

¹ No image, light blue fog
2 Magenta fog

Light blue fog
 Reaction with D260 on storage; entire film light blue

⁵ Small patches of blotch 6 Faint image with light red fog

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TABLE 2

DOW STYRON 685 AND 686 AS SUBSTITUTES FOR MX4500

Exp. No.	γ	AEI	Dmax B	Dmin B	Dnet B	$\Delta_{\mathrm{sec.}}^{\mathrm{T_r}}$	Sol. Age (Weeks
DOW STYRON	685						
1756-29-1	2.0	.36	2.17	.25	1.92	160*	-
-3	1.2	1.23	2.30	.34	1.96	140*	2
1824-3-2	1.5	.97	2.34	.22	2.12	170*	4 8
1756-29-5	2.3	1.5	2.00	.23	1.77	38	8
-8	1.6	1.3	1.85	.24	1.61	37	12
-10	4.5	1.4	2.43	.23	2.20	33	14
DOW STYRON	686						
1756-29-2	2.8	.53	2.15	.34	1.81	140*	_
-4	1.2	2.08	2.30	.36	1.94	140*	2
1824-3-1	1.2	1.07	2.14	.22	1.92	170*	4
1756-29-6	2.4	.89	2.12	.24	1.88	47	4 8
-9	2.2	1.3	1.88	.23	1.65	36	12
-11	3.5	1.4	2.46	.17	2.29	36	14

^{*} These films developed on old dichroic units. Other films developed on HID units.

25X1

25X1

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TABLE 3 TRIBROMOACETOPHENONE ACTIVATORS FOR 5/D7

No.	Compnd.	Exp. No. (1824-33-)	Amount (mg)	CBr ₄ (g)	Dmax	Dmin	* \(\text{Tr} \) (sec)	AEI (printout)	Comments
1	I	3	200	-	1.65	0.26	130	7x 10 ⁻⁵	Deep Blue Fog
2	11	6	200	-	0.88	0.32	168	4.5x10 ⁻⁵	Reddish Fog
3	I .	5	50	1.2	2.52	0.15	17	2.8x10-4	Light Blue Fog
4	II -	7	50	1.2	2.55	0.96	24	2.2x10 ⁻⁴	Deep Purple Fog

 $[\]begin{matrix} \swarrow, \swarrow, \sim \text{-tribromo-2,5-dimethylacetophenone} \\ \sim, \swarrow, \sim \text{-tribromo-4-nitroacetrophenone} \end{matrix}$

25X1

II:

All developments gave uniform high density fog with no discernible image. Other data applies to printouts. Fog colors relate to both printout and development modes and are the same in either case.

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TABLE 4

EFFECT OF MX 4500 IMPURITIES/ADDITIVES

	Exp. No. 1824-	<u> </u>	Amount (mg)	Dmax	Dnet	Gamma	AEI	$\Delta^{\!\mathrm{T_r}}$	Date	
	28-2	0,	Control	1.84	1.69	1.6	.75	52	2/24	
	32-9	0,	Control	2.20	1.96	3.0	.44	20	3/6	
	34-5	0,	Control	2.25	1.90	2.6	.30	27	3/8	
3								·		
	28-4		12.5	1.30	.97	1.6	.13	121	2/24	
	32-6		14.5	1.00	.76	· -	-	85	3/6	
	34-2		12.0	.91	.71		-	52	3/8	25X1
	28-3		5.0	1.60	1.40	1.1	.51	96	2/24	

25X1

AIR SAMPLING RESULTS COMPLETE

des results reported to us through dar. 31, 1972. Complete.

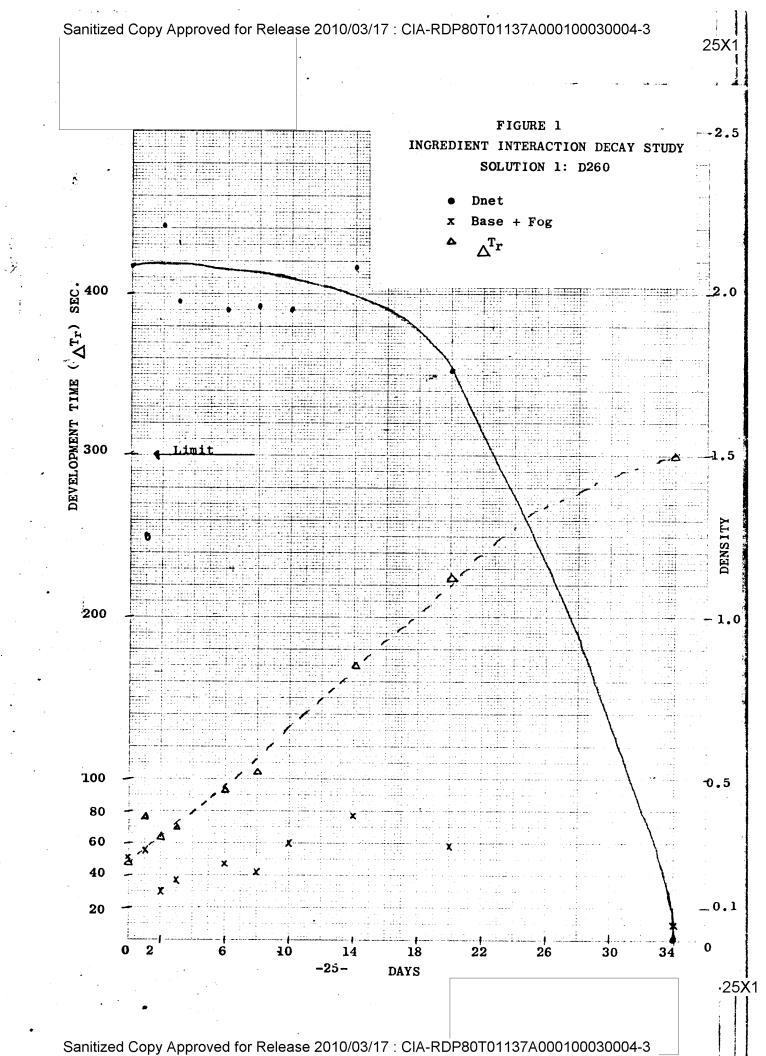
		espendant, or							
Sample Number	MO ²	Oxidants,	I ₂ ,	HC1 mg C1 /H3	HBr mg Br M3		rsenio, p/M³		
1	0-011		0.027	0.011	0.007		.0004		
. 2	35			08	.08	<	007		
3	19		ot.	90	0 8	<	Q1		•
4	20 26		07 08	1.167 08	10 07	~	007 007		
5 6	07		29	n	o8	-	02		
7	95		21.	n	08		n		
8	11			1.228	11	<	007		
9	. 17		19	26	07	<	007		
10	15		0 3	. 39	09				
11	19						OS		
12	25	0-026	25	0.640	09				
ນ	.06		-			<	007		
14 15	17 05.	23 03	12. 13	09 12	07 07 ·	•	001		
16	14	26	FFF .	0.106	08	<	007		
17	10	23	13	13	08	<	007		
18	0 7	146	15	0.139	07		Q†		
19	12	17	1 14	0.184	09	<	007		
20	07	10	18	25	06	<	007		
21	07	13	22	21	06	<	007		
22	12 10	21	20	22	_	<	007		
= 23 24	12	h9	08	13 0-360	09 09	~	007		
25	-	~		00,000		<	007	•	
# 26	18	31	09	0.128	13	<	007		•
+ 27	12	65	11	0.161	10	<	007		
+ 28	12	74	24	94	. 09	<	007		
* 29	08	95	12	5 jr	06	<	007		
* 30		52	10	51	09		Ot .		
* 31 * 32	12	77 74	n	0.119	09	<	007 01.		•
- 33	•	27		0-120 0-140	08 12		w.		
# 3L	15	18		OTTEO	**	•			
* 35	_	- 8t ₁	14	20	07	<	007		
# 36	0 8	58	19	63	11	<	007		
= 37	02	12	19	0.125	10	<	007		
● 38	07	23	16	149	08		01	•	
* 39		0.186	32	81,	0.110	۲	001		
# 10 # 10	22 24	0-099 0-154	. 09 10	0.108 0.122	0.117 0.131	< <	01. 01.		
+ 1/2	25	21	06	0.101	0.101			H ₂ Se	H ₂ Te
- ld	-	< 05	21					0.035	0.080
145	÷	37	30					0.129	0.207
+ 146		20							
47		0 6							
+ 48сн 48рф		22 37						0.148 0.139	0.024 0.136
- LBRS		بر 19						0.099	0.113
- 49CH		1.3						0.014	0.033
L 9₽Q		55			•			0.020	<0.334
→ 51CH		0.11h						6.540	0-453
51re		69		*	•			0-1109	<0.019
(=) 52CH		45						07128	0.021
52PQ (+) 53CH		143 82						0.792 I. 356	0.096 0.165
53PQR		0.100	•	1.152	0.058			4.356 1.793	0.165 0.082
* 53TUV		89		3.636	0.081			0.028	<0.017
Slichj		n		0.29	0.017			0.973	0.280
Super		Zlı		0.51	0.03			0.027	<0.017
(•) SLITER		19		0-52	0.021	•		0.008	<0.017
(+) 55013		- 29		0.61	820.0			0,008	<0.C17
SSPER		51 21.		0.55	<0.026	•			
्राक्ता (०) हास्ट्रह		34 147		072 0ግረ	0°031				
# Chain		30		0.43 0.1.9	0 20				

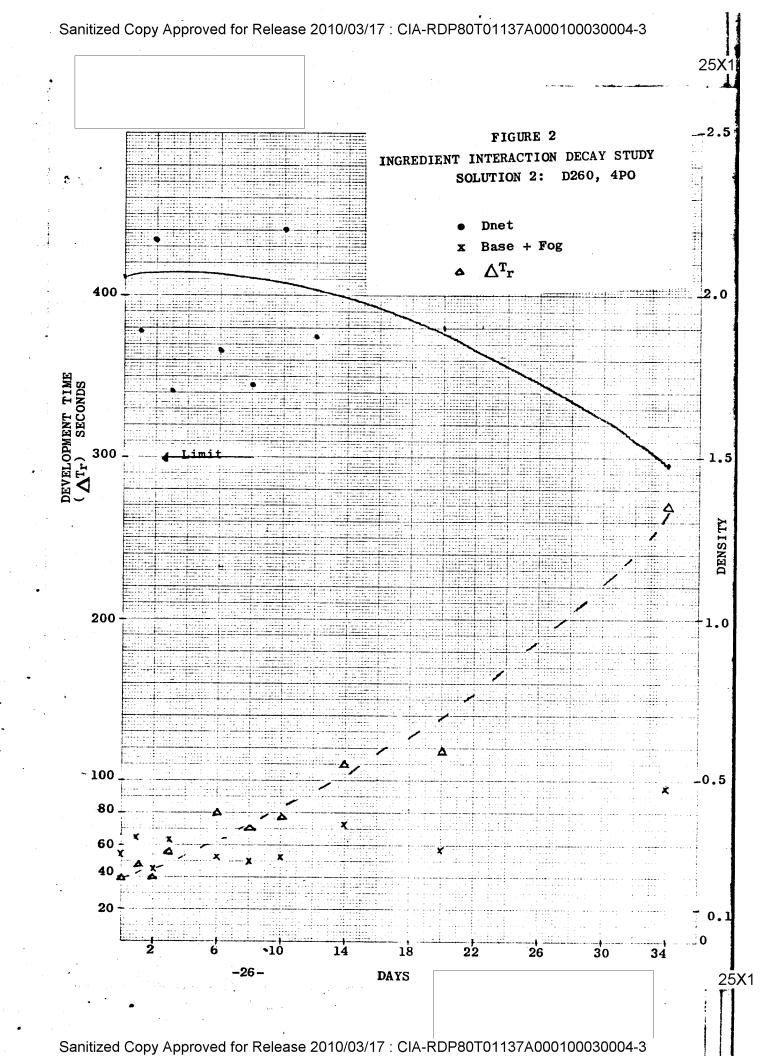
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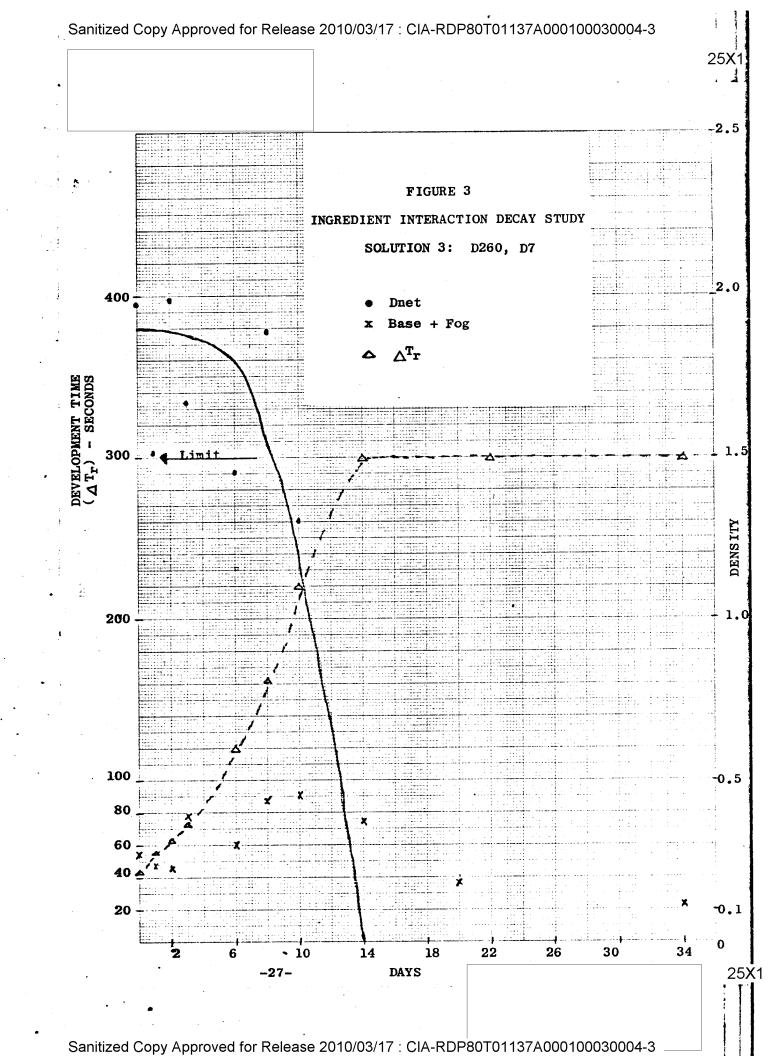
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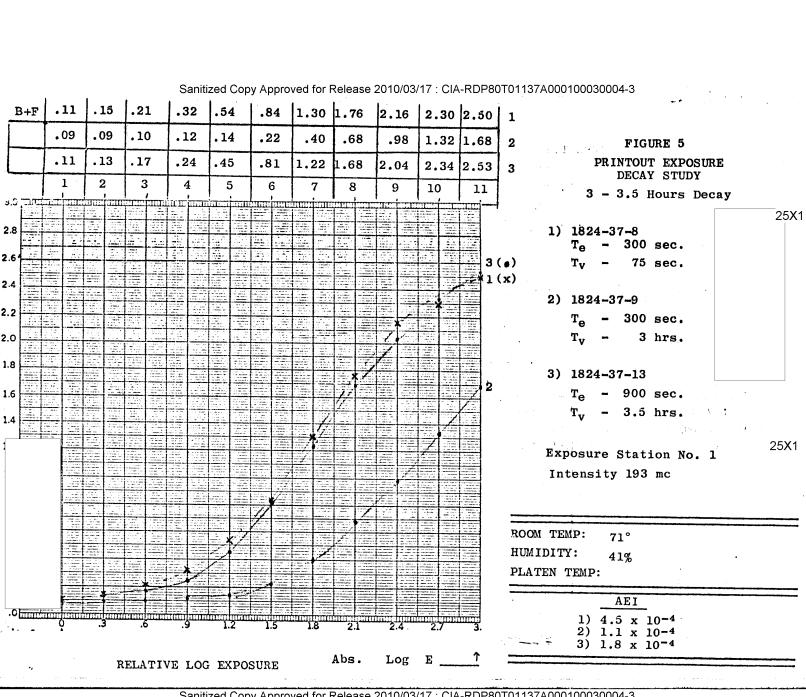
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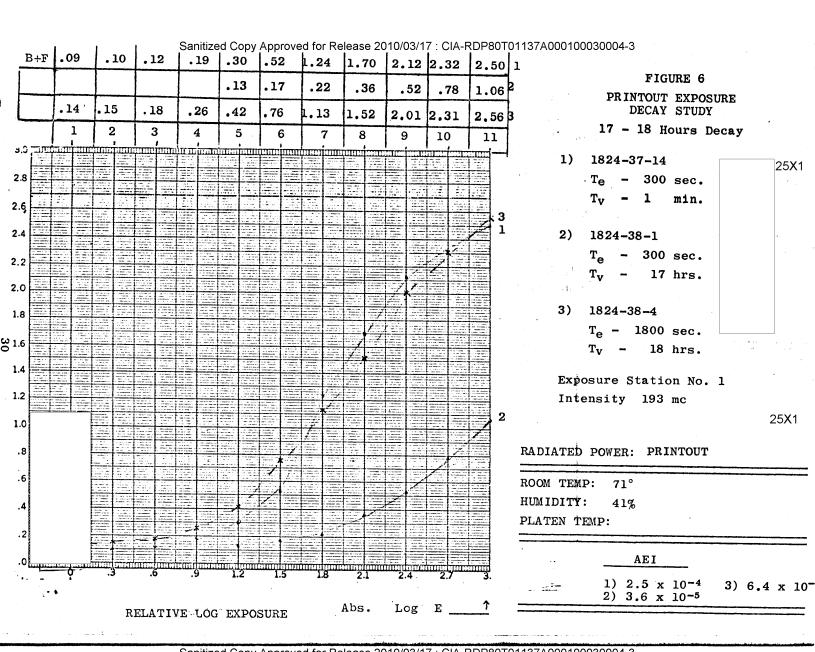
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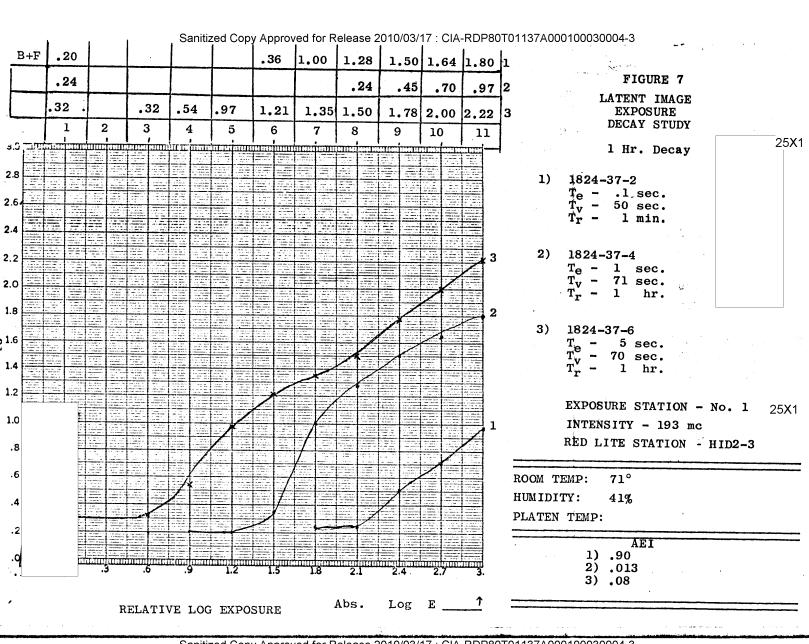


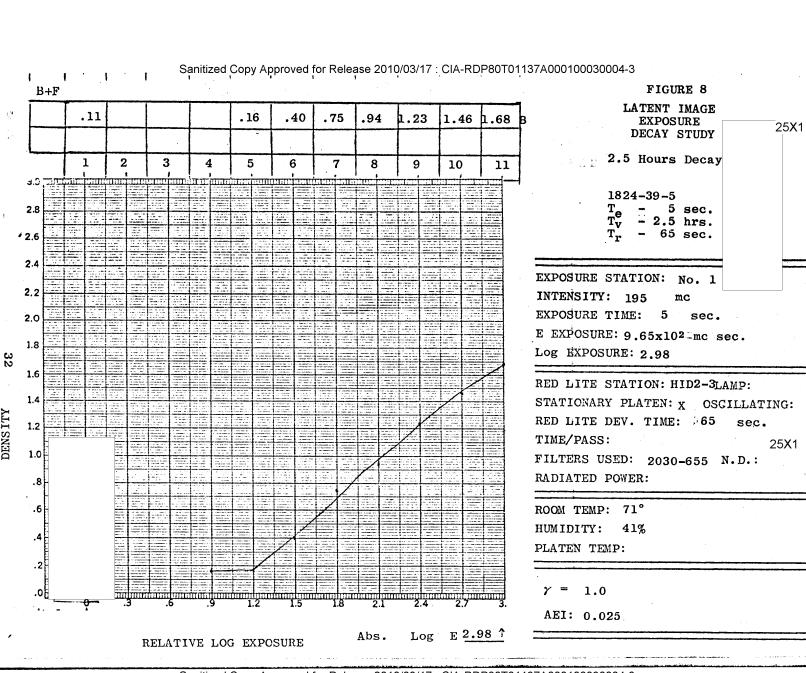




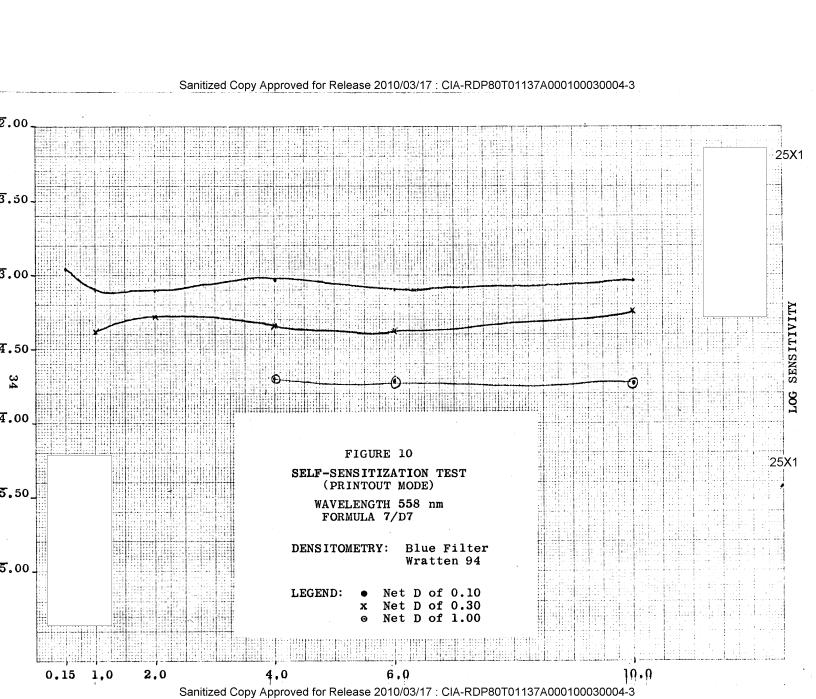


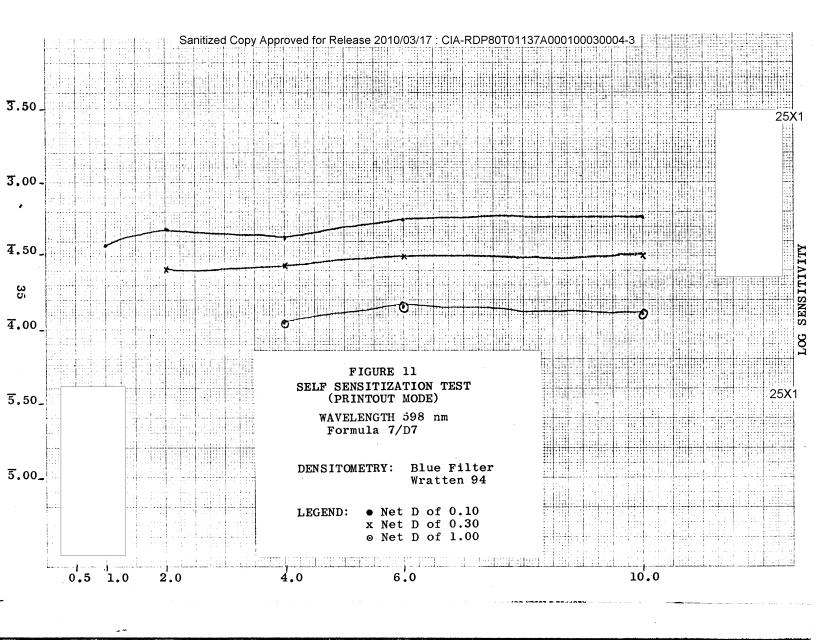




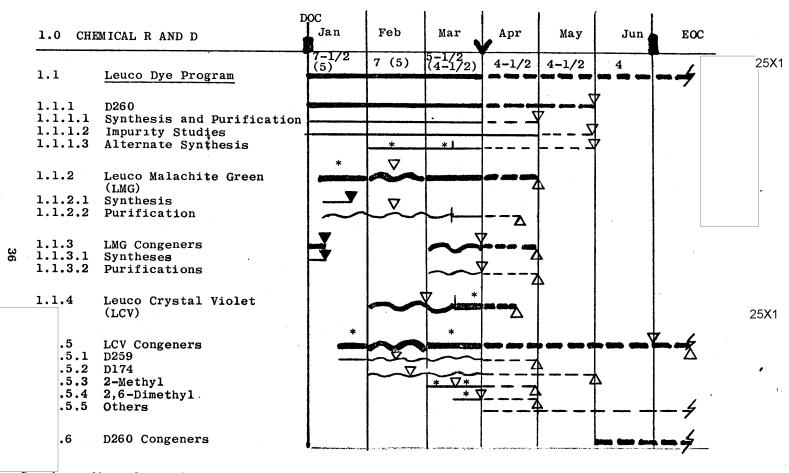


Sanitized Copy Approved for Release 2010/03/17: CIA-RDP80T01137A000100030004-3 B+FFIGURE 9 .11 .16 .25 .60 .54 .71 .71 1.00 B DELAYED DEVELOPMENT DECAY STUDY 25X1 2.5 Hours Decay 3 11 1824-39-6 2.8 Те <u>-</u> .09 sec. 75 sec. 2.6 64 sec. 2.4 EXPOSURE STATION: no. 1 2.2 INTENSITY: 193 EXPOSURE TIME: .09 sec. 2.0 E EXPOSURE: 17.3 mc sec. 1.8 Log EXPOSURE: 1.6 RED LITE STATION:HID2-3 LAMP: 1.4 STATIONARY PLATEN: X OSCILLATING: RED LITE DEV. TIME: sec. 1.2 25X1 TIME/PASS: 1.0 FILTERS USED: N.D.: RADIATED POWER: ROOM TEMP: HUMIDITY: 41% PLATEN TEMP: .8 1.07 AEI: Log E <u>1.23</u>↑ Abs. RELATIVE LOG EXPOSURE

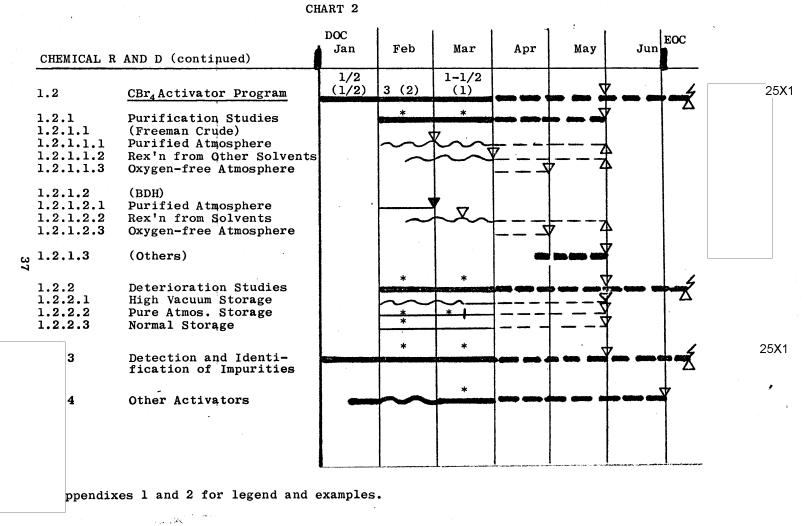




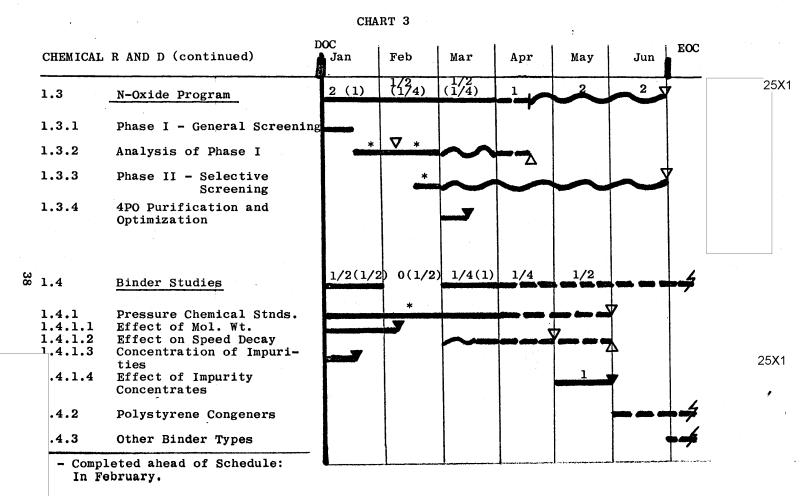
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See Appendixes 1 and 2 for legend and examples.



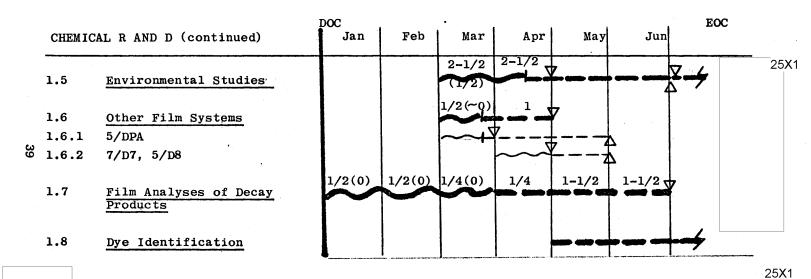
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e Appendixes 1 and 2 for legend and examples.

1. July 1880

CHART 4



ppendixes 1 and 2 for legend and examples.

	•	25 X 1

REFERENCES

- 1) Aaron and Barker, <u>J. Chem. Soc.</u> 1963, 2661.
- 2) Proposal: January 1, 1972 through December 31, 1972; Chart III, p. 49.
- 3) January Summary Report, p. 10.
- 4) February Summary Report, p. 10.
- ⁵) Ref. 2, Section 3.3.10, p. 69.

2.0 ENGINEERING

2.1 Calibration and Equipment Maintenance

Calibration and maintenance of all 325B equipment has continued on a routine basis. All equipment has been monitored, calibrated and maintained at the normal required intervals.

2.2 HID-2 Development

Completed.

2.3 Shelf Life

As previously reported, work on shelf life has been held up because of the extreme contamination found in the original engineering darkroom. A new engineering darkroom has been completed and tested and initial work begun on shelf life. A change in schedule results. Overcoating will be delayed until May 1. Reactivation began on schedule April 1. The areas to be investigated are: storage of the film in various atmospheres in the attempt to reduce deactivation of the film, and reactivation prior to exposure and processing. Many permutations on these two approaches are possible and the most promising will be pursued.

2.4 Red Light Research and Development

Work is continuing on the HID-1 and HID-2 test and evaluation programs. Performance of both units are compared based on processing conditions of the film. Filters, lamps and dichroic mirrors are updated and improved as information is obtained. Testing has shown that the previously reported filters, having a 50% cut-on at 665 nm, are nearly identical when used in all of the HID units. This allows nearly identical performance from all of the HID-1 and HID-2 units. Marc 300 lamps used in the HID-1 and HID-2 units have had a greater useful life than expected -- approximately 100% increase. They are easily replaced and quite stable through their life They are monitored periodically and adjusted during use time. to compensate for any minor changes in the lamp performance. The HID-1 and HID-2 units continue to be the primary development test bed and are performing at an excellent level.

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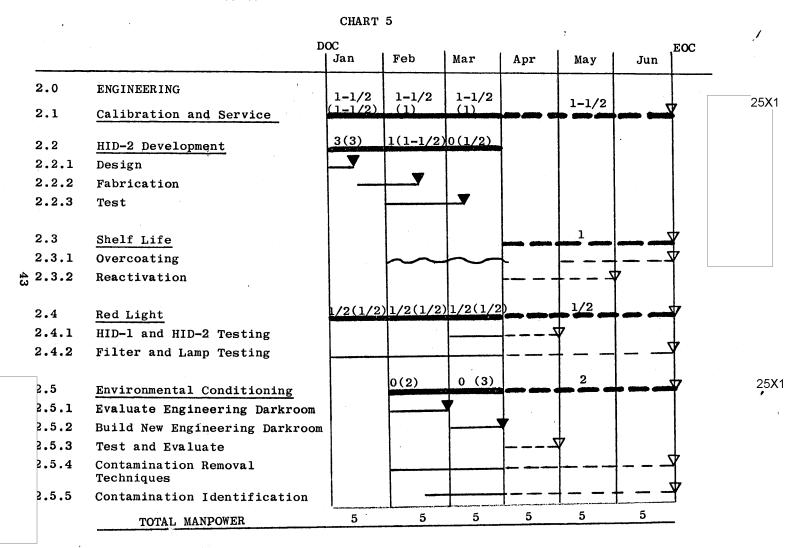
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2.5 Environmental Conditioning

The new engineering darkroom has been completed and tested to determine the effectiveness of the contamination removal system. Several modifications were necessary to the original design to improve the contamination removal. room is operated at slight positive pressure, supplied through an air scrubbing system in the interlock. Present testing has shown the contamination level in the room can be held to a level equal to the chemistry contamination-free darkroom. Initial testing showed that at times some contamination level did buildup from the surrounding environment. is continuing on better sealing techniques and the addition of an extra interlock to reduce outside contamination from entering the room each time the operator goes in and out of the room. The room is cleaned regularly and checked daily for contamination levels.

Engineering work on the shelf life reactivation project was begun only when the room was proven to be contamination free. New charcoal filtering techniques are underway to determine the optimum charcoal type for removal of this contamination. The feasibility of multiple banks of charcoal which would allow a more efficient use and cost reduction is under way.

The construction of the new engineering darkroom has proven that new rooms can be built that are contamination—free and as the need arises more can be built for the expansion of the chemistry coating group. Further work is continuing on improving the contamination removal techniques and methods for determining the contaminant. Some indication that a pollutant from the exhaust from an internal combustion engine degrades the film has been made. This will be studied to see if the individual contaminants can be identified.



See Appendixes 1 and 2 for legend and examples.

3.0 PERKIN ELMER INTERFACE AND QC/QA

3.1 Supply of Film and Equipment

3.1.1 Delivery of 325B Film

Shipment No.	Date Coated	Date Received	Time Lapse	% Fogged In Storage
1	14 Jan	17 Jan	2 Days 17 Hours	10
$ar{2}$	31 Jan	3 Feb	2 Days 17 Hours	100
	14 Feb	16 Feb	1 Day 17 Hours	30
3,4 5	1 Mar	7 Mar	5 Days 17 Hours	0
6	15 Mar	16 Mar	17 Hours	0
7	28 Mar	29 Mar	17 Hours	0

The shipment of film equipment and fix solution continues on schedule (see Chart 6). Shipments No. 6 and No. 7 both consisted of 13 sheets of hand coated film approximately 7" x 7" square approximately 40% coated. The one sample in each case that was developed for control yielded respectively an AEI 1.4 with a γ 3.8 and for Shipment 7 an AEI of 3.2 and a γ of 3.5. Shipment 8 will be produced the 17th of April. The extra week was taken here to allow Perkin Elmer extra time for analysis of their collected data.

The amount of film that has fogged in storage has been reduced to near zero. The film lost due to fogging in earlier shipments will not be made up. This has been one of the "ground rules" set up in the beginning of the project. Guaranteeing a supply of good film has the potential of shutting down the laboratory work at to concentrate on this one task. The primary concern is for a sudden loss or shortage of photograde materials.

The shipment numbers have been revised to reflect the two parts in which Shipment 3 had been delivered. The numbers now conform to the numbers being posted at P. E.'s facility.

Fred Schmidt is scheduled to visit P. E. for three days the week of April 17. The previous visits were made in January and February with a delivery of film, and equipment. Perhaps

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especially, with the state-of-the-art

3.1.2 Delivery of Solvent Rinse

familiarize,

of this project.

Sufficient supplies have been maintained at P. E.'s facility.

3.1.3 Delivery of Red Light Development Units

Two minor problems have occurred with the HID-2. They were handled over the phone and with air mail, special delivery of a replacement part in each case; the loss of time was held to a minimum of one and two days. Apparently the unit has been used considerably and the results have been satisfactory. A better determination of the operation and results from the development unit will be made during Schmidt's scheduled visit in April.

3.1.4 Cross Calibrations

The scheduled time alloted for this has been extended, as indicated on the Gant chart, because of a probable sensitometer discrepancy with regard to the resulting AEI speed numbers. There has been a very real discrepancy in apparent speed numbers which should be resolved. The film may have decayed in shipment, but a more probable cause of discrepancy is the "old" lamp still being used in the P. E. sensitometer. This will be corrected upon arrival of Shipment 8 by replacing it with a new calibrated lamp. "Old" lamps because of their shift in color show a much greater decrease in 325B film speed than the measured drop in meter candle seconds.

Figure 12 has been included here to illustrate the affect of densitometry with regard to narrow band color of light. This further enlightens the discussion in February's progress report.

3.3 Evaluation of Production, Shipping and Contamination

Production will now be performed in the new engineering enclosure. Production of filter/silicone samples, although scheduled for availability in April, will not take place, because P. E.'s current work does not require it.

Shipments are now sent via American Airlines priority parcel service. No problems have been experienced and arrival in their laboratory occurs the next morning (17 hours).

The packing methods experimented with in Shipment 5 has yielded, apparently, a superior method. The losses due to dark fogging have been reduced to essentially zero. packing method, in addition, has illustrated that even at room temperature the samples can be stored for several weeks without any measurable dark fogging. Of course, these samples have still decayed with respect to speed. By extending the exposure time the film still can be image-wise exposed to yield approximately the original Dmax and curve shape. The success of developing these decayed, room temperature samples has not been as clear cut. Preliminary tests were done to show that development was possible even in the most decayed samples after four weeks of storage at room temperature. A preliminary revival test was performed by soaking the film samples in benzene vapors for two hours. This increased the amount of development possible although the tests were not done in a quantitative The possibilities of reviving film will be studied in a more detailed way by Engineering. The implications of the unfogged, room temperature film were discussed in the Chemistry Section 1. 10.2.

The tentative explanation for the lack of dark fogging in the wrapped samples is that the dark fogging is also dependent on air contamination. Samples stored in the open air of the "clean" room showed visible dark fog after only a few hours. This explanation would still be compatible with the earlier hypothesis (see January progress report Section 3.0) that removal of 0_2 , e.g. 100% Argon or 100% CO_2 , cause dark fogging also.

The three sets of air samples taken at P. E. show that their air with regard to the contaminant levels measured at H.R.I. is low. Some of the results (Table 6) are plotted in the frequency diagrams in Section 3.7.

3.4 Monitoring of Results and Anticipation of Subsequent Plans

The change of 325B project personnel at P. E. has resulted in a setback in progress. The two new people are performing at a higher level now and have accomplished some shelf life tests. The test plans that P. E. originally put together for use of P. E.'s environmental chamber has been postponed.

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trip scheduled for April should help clear up some of the questions that have been brought up by the new P. E. people. Some key observations concern subtle effects which are hard to monitor over the phone. The comparison of P. E.'s results with the current observation here with the current materials often times can facilitate interpretation of results.

3.7 QC/QA

Material supply (see Table 7) has continued without any serious problems with respect to shutting down the coating work. The synthesis and purification chemists are supplying minimum acceptable materials in order to reduce the cost of time and materials. They are showing significant progress in increasing the efficiency of production of photograde materials. The bare minimum usable for most of the routine chemistry work includes a Dmax of 2.0 and an AEI speed of 1.0 and variable γ . The γ 's are of small concern since there are a variety of ways to approach this parameter. A Dmax of 2.0 is the first indicator to suffer when materials are of poor quality.

A statistical breakdown was made of one of the better recent samples, plotted in Figure 13. Dmax was acceptable at The speed was especially good at 4.5. The γ was especially good, 1.6; but, the curve shape shows the γ to be located very near to the toe of the curve. When this is broken down onto a frequency chart, Figure 14, one can see that the high quantum efficiency appears very early in the production of the image and the QE with respect to the time intervals shows a skew to the left. This curve shape, therefore, shows that image production starts off almost explosively and then tails off. The more classic case of an "S" shaped D-log E curve is the result of a normal bell-shaped distribution of quantum efficiency vs. time interval (see Figure 15). The skewed shape is not uncommon in the polymer chemistry. The situation is controllable by a variety of methods, such as temperature control and concentration of reactants.

In general the quality of data generated has been maintained. The gross estimated error in consistency at this time is probably the placement of the densitometer on the individual steps of the tablet. This can have a significant effect, i.e. .2 density units between operators when the materials are marginal and the development is pushed to the limit.

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The study of the air contamination problem has been updated with the most recent gas analyses, which have now been received in their entirety from National Loss Control Service Corp. (see Section 1.5). Note that the HBr data splits into two. As of Sample 39, all the measured amounts fall into a completely different range without regard to "good" or "bad" film days. The break in the data indicates strong possibility of a change in the analytical method used. This means the P. E. HBr data should be compared only to the data after No. 39. interprets the data to yield a relatively positive indication that oxidants, in particular HBr and HCl (Figures 16 and 17) are the primary contaminants. This fits into past studies that have shown HBr, HCl and acids in general to have a very deleterious affect on storage life of solutions of the various combinations of ingredients used in our film formula. In other free radical film projects acids have also been identified as very deleterious In a very preliminary test a car exhaust was to the solutions. found to be a contaminant generator. The film was quickly contaminated with a minimum amount of car exhaust in the immediate vicinity of the engineering darkroom. Without further regard to identification of specific contaminants, the car exhaust will be used as a contamination generator for the purpose of identifying gross methods of reducing contamination, e.g. charcoal filters, dust filters, counter-current water wetted packed columns, or slightly basic water columns.

The use of Barnebey Cheney charcoal units are usually satisfactory. The purchase of new units has been delayed by apparent problems at the Barnebey Cheney factory. There also has been a delay in the feedback of checking the life of the charcoal samples retained each time the set of filters are replaced in the units.

A QC/QA notice was issued to all personnel in the coating areas and purification areas of photograde materials: Use disposable booties, paper hats and lab coats. In addition throw rugs were placed in key areas in and around the laboratory. There are now several QC/QA notices with regard to maintaining personnel and material standards in the film production areas.

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CONTAMINATION ANALYSES OF AIR SAMPLES TAKEN AT PERKIN ELMER February 16, 17, and 18, 1972

TABLE 6

Oxidants	Chlorides	Bromides
$mg 0_3/M^3$	mg Cl/M ³	mg Br/M³
0.047	0.35	0.020
0.039	0.4	0.020
0.019	0.48	0.019

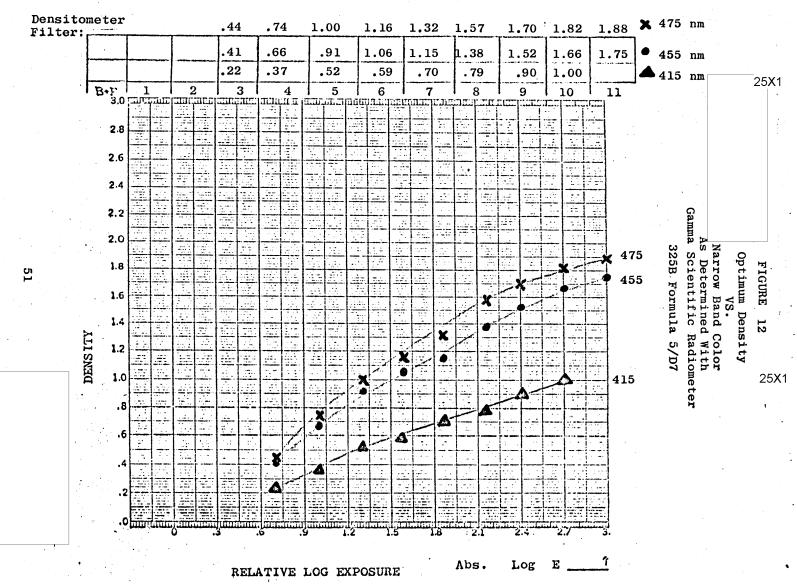
TABLE 7
MATERIALS INVENTORY
7 APRIL 1972

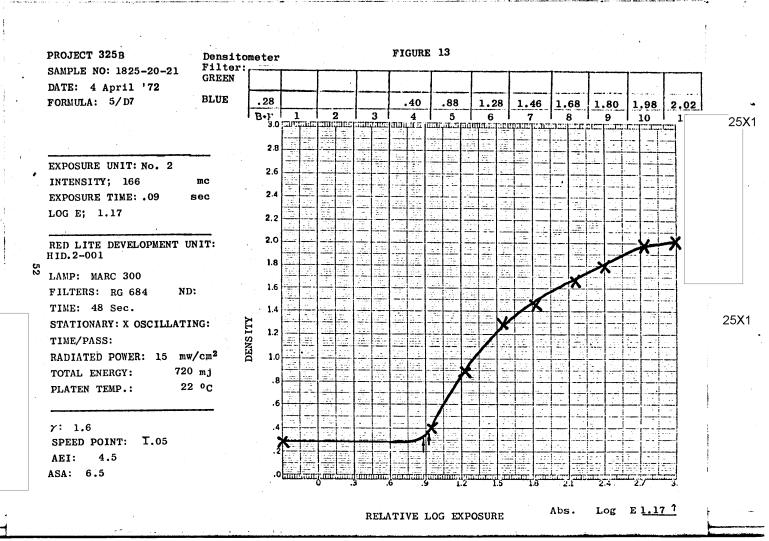
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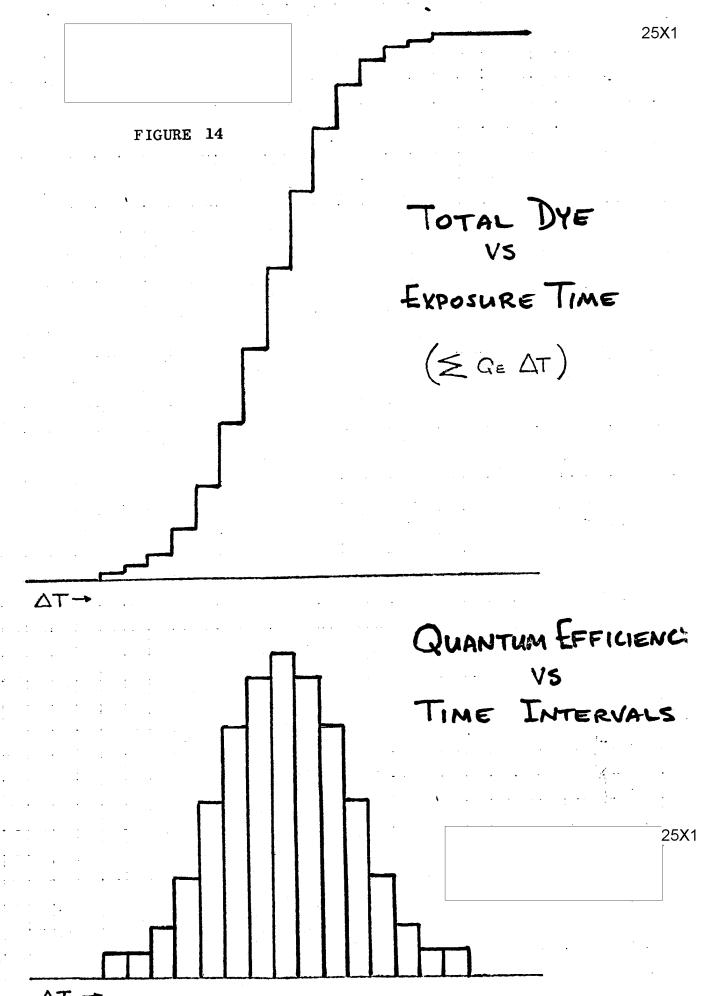
FORMULA 5/D7 **PHOTOGRADE** AMOUNT LEAD ON HAND NEEDED TIME FOR IN EQUIVILENT PER COATING PHOTOGRADE CRUDE PHOTOGRADE COATINGS ON HAND GMS. OR CC. ON HAND FROM CRUDE D-260 676 .0444g. 30g. 1000g. 2 DAYS CBr_4 760 .623g. 473g. 7kg. 4 DAYS FOR FREEMAN IMMEDIATE FOR FRENCH 4,500 P.O. .0089g. 200g. 40g. 4 DAYS 25X1 D-7 .0284g. 14k 400g. UNLTD. IMMEDIATE POLYSTYRENE 100k 1/2g 50kg. UNLTD. IMMEDIATE 25k BENZENE 2cc. 50 liters UNLTD. IMMEDIATE

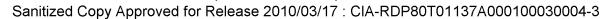
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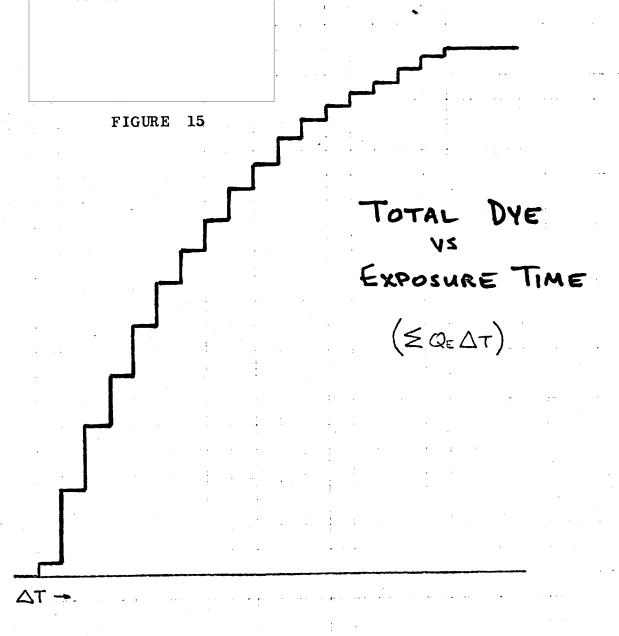


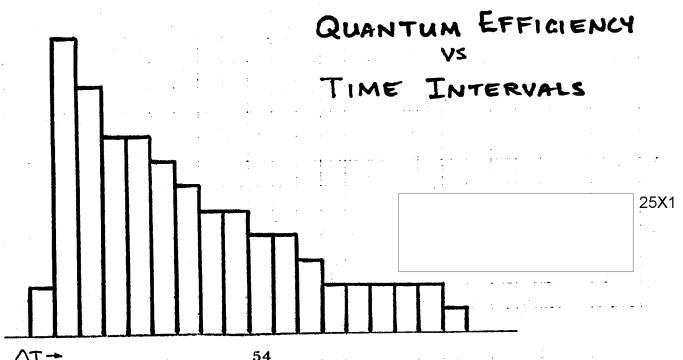




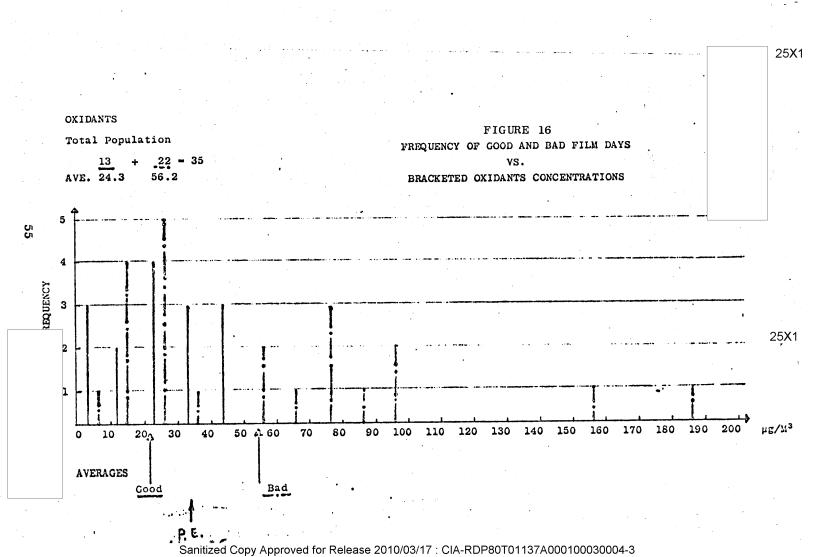








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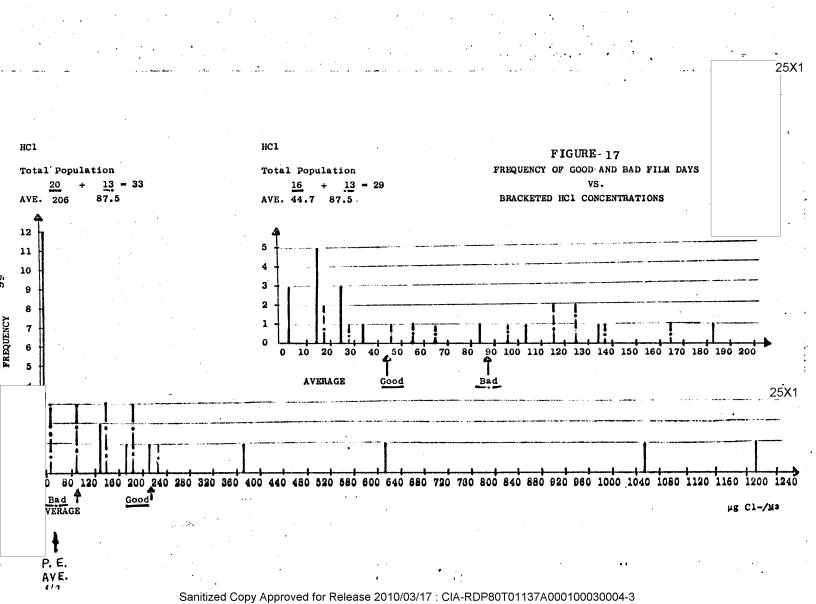
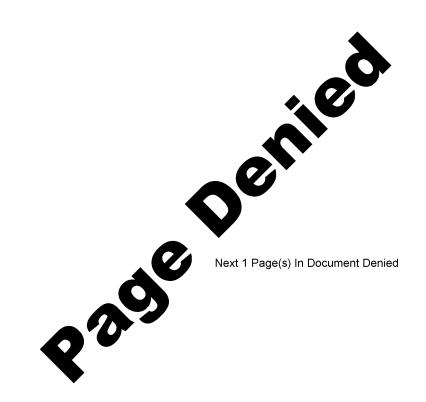


CHART 6 DOC EOC Feb Jan Mar Apr May Jun 25X1 3.0 P.E. INTERFACE AND QC/QA 1/2 1/2 3/4 1/2 1/2 3.1 P. E. Interface $\nabla \cdot \nabla$ $\nabla \nabla$ $\triangle \triangle \triangle$ 3.1.1 Film Shipment ∇ ∇ 3.1.2 Solvent Rinse 3.1.3 4B RLD Unit 3.1.4 HID-2 Unit 25X1 3.2 Cross Calibrations P.E. 3.3 Evaluation of Production, 57 Shipping Contamination 3.4 Monitor Results Participation In Subsequent Tests Plans 3.5 Optimize Results and Special Tests at Both Facilities 25X1 3.6 Reports 1/2 1/4 1/2 1/2 1/2 1/4 3.7 QC/QA TOTAL MANPOWER

See Appendixes 1 and 2 for legend and examples.

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ROBLEMS					
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inability to it	ichtily ull 50	,			
				•	
ANS FOR NEXT REPO	RTING PERIOD				
Continue projec	ct work along	forecast	schedule;		
pick up slippage	in various t	asks.	·		
INANCIAL				•	
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APPENDIX 1 LEGEND FOR GANT CHARTS 1 THROUGH 6

HEAVY LINE: Major Section and Major Subsections

THIN LINE: Subsections (Tasks)

Solid Line: Completed to date

Dashed Line: Remainder of forecast period plus extension(s)

Wavy Line: No work performed

1) though originally forecast

2) subsequent to existing date indicates will be abandoned

without immediate plans for rescheduling

▼ Forecast completion date
 ▼ Completed on schedule
 Δ Extended completion date
 Δ Completed extension

Task performed but at lower level of effort than forecasted

Extended into second six months

1,2 ect. - Explanatory note (see bottom of page)

x(y) x = Forecast manpower loading <math>y = Actual manpower loading Major Sections only

25X1

EXAMPLES FOR GANT CHARTS 1 THROUGH 6

